Short communication

Preparation of reduced tantalum pentoxide by electrochemical technique for oxygen reduction reaction

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HIGHLIGHTS

- An electrochemical reductive treatment was successfully applied to reduce Ta_2O_5 deposited on a glassy carbon.
- The electrochemical treatment also resulted in morphological changes of the deposits.
- The treated TaO_x exhibits a high ORR activity in acidic solutions.
- The reduced oxide possesses a four-electron ORR electrocatalysis at potential above 0.8 V.

ABSTRACT

A non-Pt based electrocatalyst, tantalum oxide (TaO_x) deposited on glassy carbon, for oxygen reduction reaction (ORR) in acidic solutions was prepared by electrochemical technique. The tantalum pentoxide (Ta_2O_5) formed on the as-prepared deposits was electrochemically reduced to generate its reduced species which conventionally need a heat treatment under H_2 atmosphere. The reduced Ta_2O_5 shows a fairly high onset potential of ORR (0.87 V vs. RHE) in comparison with that (0.98 V) at a commercially available Pt/C catalyst. The ORR performance of the TaO_x was investigated using a rotating ring-disk electrode voltammetry showing that a four-electron ORR takes place actually at potential above ca. 0.8 V and a two-electron ORR becomes significant gradually as the potential is increased negatively.

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1. Introduction

In the light of changing of energy policy which turns to renewable resources and in order to reduce greenhouse gas effects, the emergence of clean technologies has been an important issue. One of their examples is proton exchange membrane fuel cells (PEMFCs) which have still a major problem for commercialization due to the scarcity and high price of Pt used as electrocatalysts. Particularly at the cathode where oxygen reduction reaction (ORR) takes place, it is even more challenging because the poor stability of Pt nanoparticles supported carbon (Pt/C) catalysts at a high potential (>0.8 V) demands a huge amount of them to keep the performance for a long period of operation [1]. Therefore, the development of non-Pt catalysts for the cathode has been rapidly increased in the last decade. For instance, tantalum oxide (TaO_x)—

based materials would be promising alternatives since they can sustain in acidic environments and have been found as active electrocatalysts for ORR [2–5]. The presence of oxygen vacancies in the oxides is strongly suggested to play a pivotal role in the electrocatalytic reaction because they may enhance the electrical conductivity as well as serve as the active sites for O_2 adsorption [4–10].

Oxygen vacancies of metal oxide are well known to determine the chemical and electronic properties of the oxide and are associated with oxygen-deficient d^0 or reduced oxides with a low number of electrons filled in the d bands [9–11]. Conventionally, to produce such oxide phases, the oxides which are usually in their stoichiometric forms, e.g., Ta_2O_5, are calcined under a reduced atmosphere, e.g., pure H_2 or at extremely high temperature with the absence of O_2. These techniques have been routinely used, for example by Ota et al. [4,5] and Domen et al., [3], to prepare active metal oxides-based electrocatalysts (TaO_x, NbO_x, ZrO_x, etc.) for ORR with highly positive onset potentials (>0.8 V vs. RHE). However, a high temperature of calcination particularly under pure H_2 gas not

only results in a high cost and safety issues but also usually causes a sintering of nanoparticles leading to a loss in their active surface area and nature. Moreover, because of the technical difficulties arising from this conventional method [3], the rotating-ring disk electrode (RRDE) voltammetric measurements are difficult actually, although the obtained results are very useful in clarifying ORR mechanism, typically on whether a four-electron ORR process takes place or not.

In this communication, we demonstrate a new technique for fabrication of TaO_x-based electrocatalyst for ORR in which the TaO_x was electrodeposited on a glassy carbon (GC) electrode (TaO_x/GC). Instead of using calcination techniques as mentioned above, we attempted to employ an electrochemical reductive treatment to generate a reduced species of the Ta_2O_5. This facile, inexpensive and simple method has successfully produced an active TaO_x for ORR electrocatalysis and easily allowed us to investigate its activity using RRDE voltammetric measurements. To the best of our knowledge, this is the first attempt to apply the electrochemically reduced Ta_2O_5 as ORR electrocatalyst.

2. Experimental

For fabricating the TaO_x/GC electrode, there are only two required steps. The first one is the electrodeposition of TaO_x, and the detailed procedure basically follows our previous work [12]. Briefly, a cleaned RRDE electrode (GC disk:6 mm in diameter) was connected into a conventional three-electrode electrochemical cell which contains Ta solution. An Ag wire was used as a quasi-reference electrode, and a GC plate as a counter electrode to avoid Pt contamination. The solution was prepared by firstly dissolving 0.179 g of $TaCl_5$ (Alfa Aesar) and then 1.06 g of $LiClO_4$ (Wako Pure Chemicals) in 10 mL of propylene carbonate (PC, Kanto

Chemicals) solution. The bath solution was vigorously degassed by Ar bubbling for 15 min. A cyclic voltammetry (CV) technique was utilized for the deposition of Ta in which the potential was scanned between 0.3 and -2.0 V vs. Ag wire at scan rate of 20 mV s^{-1} for 2 cycles giving about ~29 μg cm^{-2} of Ta. Immediately after the deposition, the electrode was successively immersed in methanol and water for 1 min each to remove the remaining solution. As the second step, to mimic the heat treatment under H_2 atmosphere in producing the reduced Ta_2O_5 species, we introduced an electrochemical reductive treatment in which the Ta-deposited electrode was potentiostatically poised at potential of -0.6 V for 12 h (as the optimum condition). This was then followed by performing a CV in the potential range of -0.2 and 1.3 V at 50 mV s^{-1} for 10 cycles for electrochemical treatment before ORR measurements. As a control experiment for anticipating the contribution of (if any) impurities deposited during electrolysis, the same electrochemical procedure was also carried out for the bare RRDE at which the ORR performance was examined for comparison.

All the electrochemical experiments were performed using a three-electrode electrochemical cell by operating ALS/CHI Electrochemical Analyzer (Model 760 Ds) at room temperature (set at 25 °C). For electrochemical characterizations including RRDE voltammetric measurements, a Pt wire was used as a counter electrode and an Ag|AgCl|KCl$_{(sat)}$ was served as a reference electrode and all the potentials reported here are given with respect to a reversible hydrogen electrode (RHE). For ORR comparison, a good quality of thin film of a commercially available Pt/C (Pt: 46.6 wt. %) purchased from Tanaka Kikinzoku Kogyo Corp., Japan (TKK) with loading of 10 μg$_{Pt}$ cm^{-2} was used and the details of its preparation were given in our previous report [13]. Briefly, a 30 mg of the Pt/C was weighted and poured into a 25 mL vial. A 21 mL of 67% iso-propanol solution was prepared and then it was transferred into the
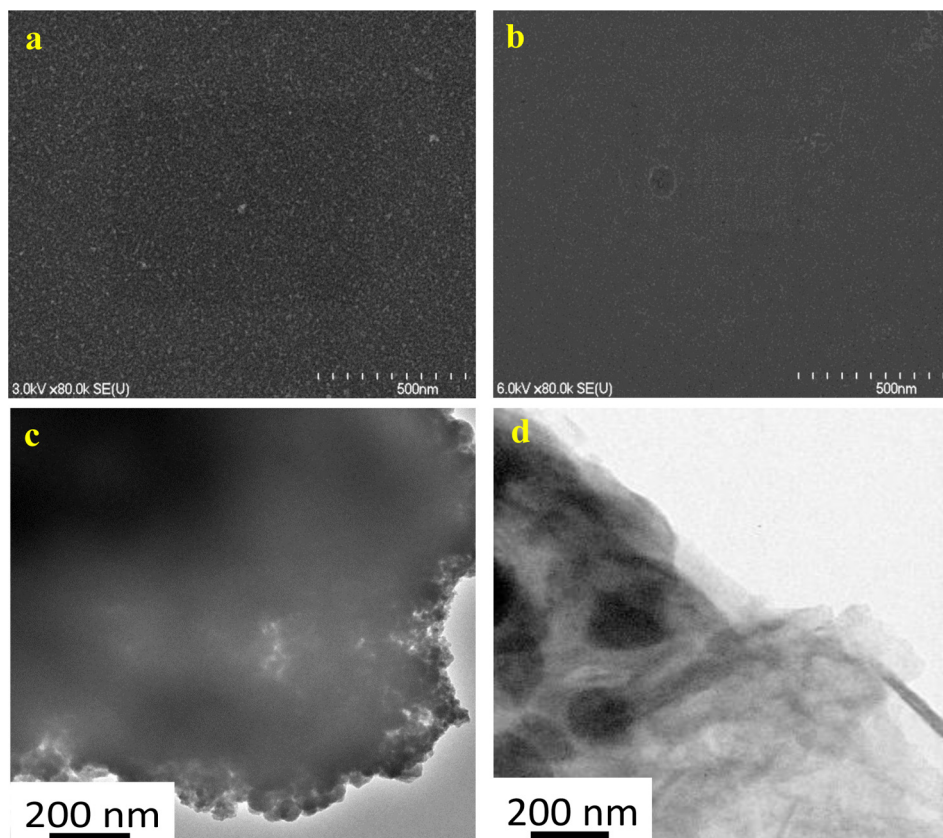

Fig. 1. (a and b) SEM and (c and d) TEM images taken at the TaO_x/GC electrodes (a and c) before and (b and d) after the electrochemical reductive treatment.

vial followed by ultrasonication for 60 min. A 1.08 mL of this suspension was dropped into a 5 mL vial and then 3.92 mL of the 67% isopropanol solution was added. A 20 μL of 5 wt. % Nafion solution was added and ultrasonicated for 30 min. Then, a 20 μL of the Pt/C suspension was casted onto the polished GC disk electrode and dried using a slow flow of hot air.

For their physical characterizations, XPS spectra of the TaO_x/GC electrodes before and after the electrochemical treatment were acquired using an ESCA 3400 electron spectrometer (SHIMADZU) with unmonochromatized X-ray source (Mg Kα (hυ = 1253.6 eV) anode, emission current: 20 mA, and acceleration voltage: 10 kV). In order to compensate the electrostatic charging effects, a C 1 s spectrum at binding energy of 284.5 was used as our internal reference. The surface morphologies were examined using a field emission scanning electron microscope S4700 (HITACHI) and JEM-2010F (JEOL) for SEM and TEM measurements, respectively.

3. Results and discussion

Fig. 1 shows (a and b) SEM and (c and d) TEM images of the TaO_x/GC electrode before and after the electrochemical reductive treatment. In the SEM images, we can clearly see that in the as-prepared electrode (Fig. 1(a)), the TaO_x deposits are homogeneously dispersed on the substrate as indicated from the uniform particles size (between 20 and 30 nm) and consequently, the appearance of these particles forms rough surfaces. After the electrochemical reduction (Fig. 1(b)), the size of deposits becomes smaller with smooth appearance and no distinct particle shapes are observed being distinct from the as-prepared electrode. Fig. 1(c) and (d) display the TEM images for the TaO_x/GC electrode before and after the electrochemical treatment, respectively. Again, here we can see that in the as-prepared electrode, the TaO_x deposits form as agglomerated particles with approximate size of 30 nm and after the treatment, they turned to a more transparent layer with no distinct particles size and shape suggesting that the deposits might become thinner.

The examination of the chemical states of Ta in the TaO_x/GC electrode before and after the electrochemical reductive treatment was carried out based on its XPS measurements. Fig. 2(a) shows the deconvoluted Ta 4f spectra for the TaO_x/GC electrode before and after the electrochemical reduction. In the as-prepared TaO_x/GC electrode, only one set of peaks at binding energies of 28.7 and 26.8 eV attributed to Ta_2O_5 of Ta $4f_{5/2}$ and Ta $4f_{7/2}$, respectively, was acquired after the deconvolution, being consistent with previous works [3,12,13]. In the case of the treated TaO_x/GC electrode, the peaks apparently shifted to the lower ones at 28.2 and 26.3 eV (or by 0.5 eV), indicating a reduction product of the Ta_2O_5 with Ta of oxidation state less than 5+ which was also found for the case of reduction by heating under H_2 atmosphere [3,14] and no additional peak was obtained because no enlargement of full width at half maximum (FWHM) value of the spectra was observed. In previous work [15], it has been found that the TaO_2 is located at binding energies of 27.2 and 25.3 eV for Ta $4f_{5/2}$ and Ta $4f_{7/2}$, respectively which are much lower than those for the reduced Ta_2O_5. Meanwhile, recently, Matsumoto et al. [16] have reported that at the Ta−CNO, besides Ta^{5+} of the stoichiometric Ta_2O_5, the lower binding energy peaks (by 0.4 eV) ascribed to Ta atoms in TaO_x with oxygen vacancies are observed using hard X-ray photoelectron spectroscopy and it is identical with our present results. Thus, we could conclude that the reduced Ta_2O_5 with the binding energies at 28.2 and 26.3 eV is attributed to the Ta_2O_{5-y} $(0 < y < 1)$. The lower binding energy of this species compared to that of the stoichiometric Ta_2O_5 is owed to the less positive charged Ta due to oxygen vacancy sites [16]. The peak of O 1s spectrum (Fig. 2(b)) was also found to shift the lower binding energy by about 0.9 eV compared

to that of the as prepared electrode, also supporting the above mention. Furthermore, it is also interesting to notice that the intensity of the Ta 4f and O 1s spectra at the treated TaO_x/GC electrode increases almost three times compared to that at the as-prepared electrode which could be a result of the morphological changes as shown in Fig. 1.

Next, we investigated the ORR performance using a linear sweep voltammetry (LSV) in O_2-saturated 0.1 M H_2SO_4 at a low scan rate (5 mV s^{-1}) and onset potentials were obtained as a potential at which the cathodic current reached 2 μA cm^{-2} in respect to the backgrounds. Although the measurements in this electrolyte are unfavorable for the Pt-based catalysts due to adsorption of the sulfate anions, we were encouraged to use this electrolyte to compare the present results with the previous ones [2−5]. As seen in Fig. 3(a), a facile ORR activity of the Pt/C is observed as indicated by the onset potential of 0.98 V and a sharp cathodic peak located at 0.8 V. A fairly high ORR onset potential of 0.87 V was also obtained at the treated TaO_x/GC electrode which is close to those (0.92 [3] and 0.94 [4,5]) reported for TaO_x-based electrocatalysts prepared using the conventional calcination method. This slight difference might arise from the roughness factor and the nature of supporting materials which affect the active surface area and conductivity, respectively. Meanwhile, as expected, the bare GC electrode, which was also treated by the same electrochemical treatment as that used for the TaO_x/GC electrode, has no ORR activity in this potential
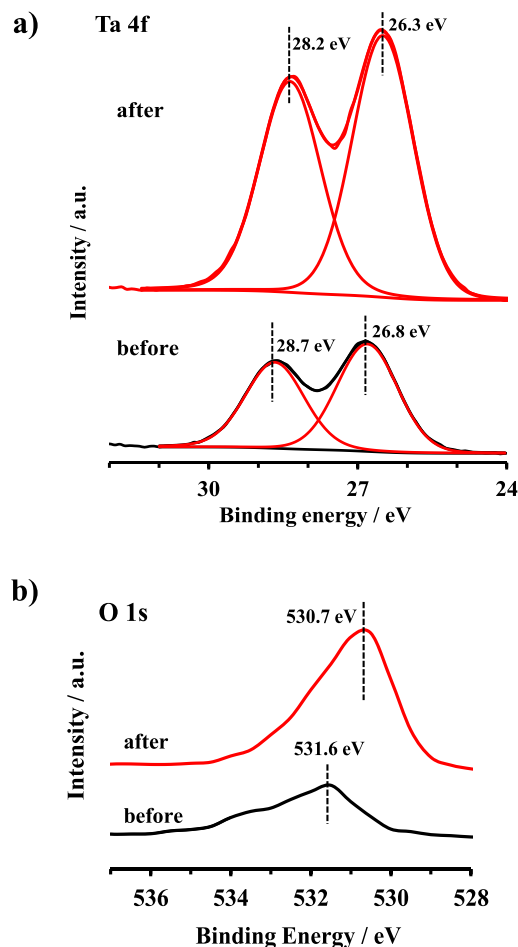

Fig. 2. XPS (a) deconvoluted Ta 4f and (b) O 1s spectra of the TaO_x/GC electrode after and before the electrochemical reductive treatment.
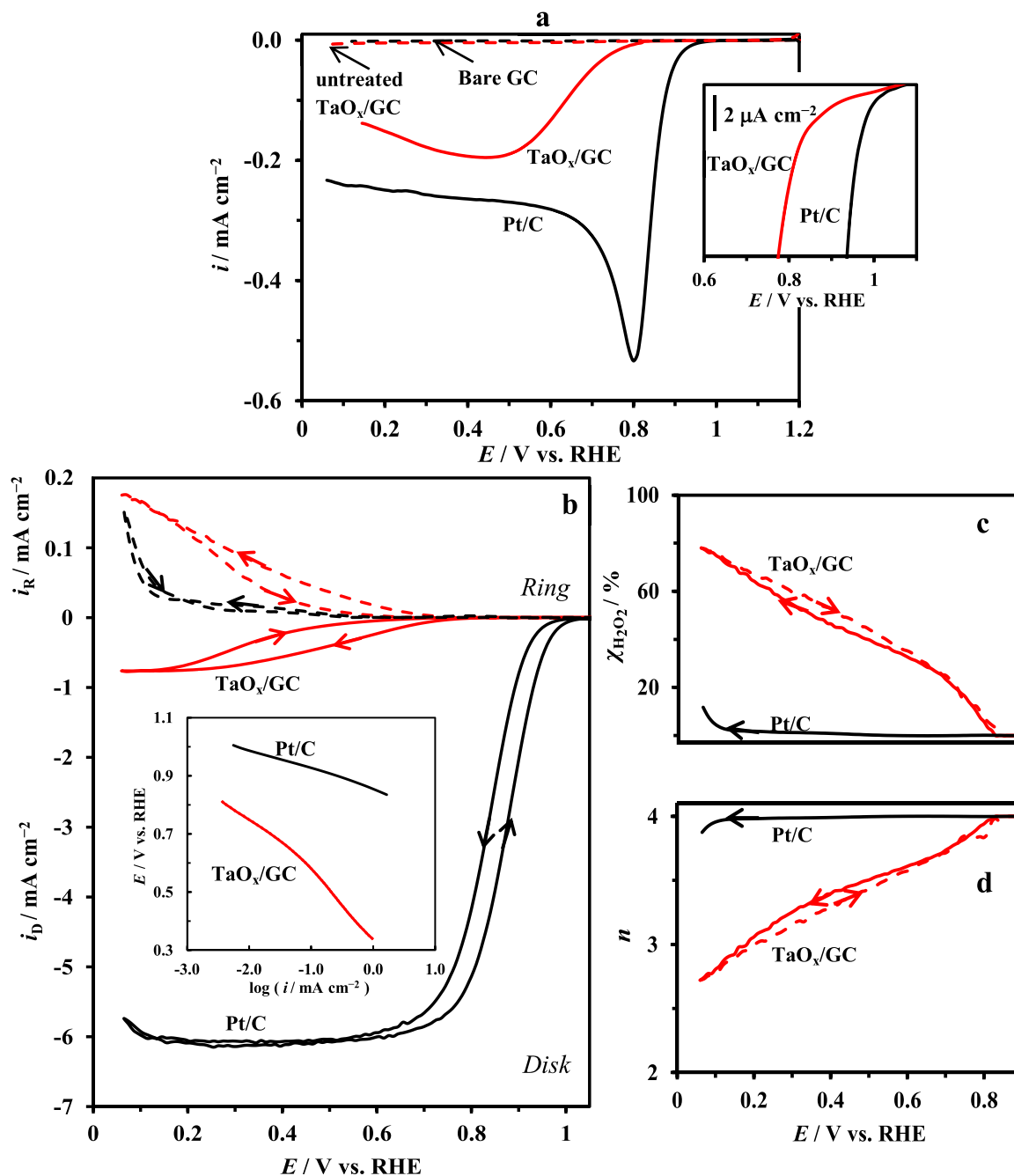
Fig. 3. (a) Linear sweep voltammograms (after background subtraction) obtained in O_2-saturated 0.1 M H_2SO_4 solution at scan rate (v) of 5 mV s^{-1} (b) RRDE voltammograms (after background subtraction) obtained at v = 10 mV s^{-1} and rotation rate of 1600 rpm in O_2-saturated 0.1 M $HClO_4$ solution. The inset shows the mass transfer-corrected Tafel plots (obtained at the cathodic scan). (c) Percentage of H_2O_2 ($\chi_{H_2O_2}$) produced at the disk electrodes. (d) Number of electrons (n) transferred during the ORR.

region, demonstrating that the observed ORR performance at the treated TaO_x/GC electrode is not due to any impurities, but contributed to the ORR activity of the TaO_x itself. The untreated TaO_x/GC electrode also showed no reduction peak in this potential region, possibly due to the thick deposits and the presence of insulating Ta_2O_5 layer which hinders the electron transfer for ORR.

The ORR activity of the TaO_x catalyst was then examined using an RRDE voltammetry and the typical results are shown in Fig. 3(b). In this case, the electrolyte was changed from 0.1 M H_2SO_4 to 0.1 M $HClO_4$ solution to fairly compare the ORR performance of the TaO_x/GC and Pt/C electrodes, because a lower energetic adsorption of ClO_4^- anions will be negligible in affecting their ORR activity. At the

Pt/C electrode, a well-defined RRDE voltammogram with the mass-transfer limited current of ~6.0 mA cm^{-2} and a very low current intensity at the ring electrode are obviously observed in an excellent agreement with commonly obtained results supporting a four-electron process of ORR [12,13,17]. At the treated TaO_x/GC electrode, on the other hand, although the onset potential is fairly positive (0.87 V), a much lower limiting current (~0.8 mA cm^{-2}) at the disk electrode and a significantly high ring current (especially at potential < 0.5 V) are observed. A low intensity of the cathodic current on the rotating disk electrodes was also observed by other groups and was ascribed to the insulating property and diffusion resistance of the TaO_x [2,18,19]. The mass transfer-corrected Tafel

plots for the voltammograms obtained at the cathodic scan are shown in the inset of Fig. 3(b) and it is apparent that the TaO_x/GC electrode possesses a considerably larger Tafel slope than that of the Pt/C one, for example, at the low current density region (-0.03 and -0.3 mA cm^{-2}) the Tafel slopes of -142 and -62 mV dec^{-1} were obtained for the TaO_x/GC and Pt/C catalysts, respectively. Furthermore, we then calculated the percentage of H_2O_2 produced at the disk electrode (χ_{H2O2}) and the number of electrons transferred (n) in the ORR in accordance with the formulas provided in Ref. [17], as shown in Fig. 3(c) and (d). The Pt/C electrode actually possesses a four-electron ORR performance in the examined potential region as also indicated from the low H_2O_2 production. At the TaO_x/GC electrode, however, at potential above 0.8 V the ORR is close to a four-electron process, but below this potential, the (χ_{H2O2}) and n apparently increases and decreases, respectively, as the potential is increased negatively; for example $\chi_{H2O2} = 75\%$ and $n = 2.75$ at 0.05 V. Another important feature is the dependence of the ORR performance upon the potential scan direction in which the ORR activity of the TaO_x/GC electrode in the cathodic scan is significantly higher than that in the reverse scan, suggesting that in the oxide (or the so-called "partially oxidized" [4,5]) form, the TaO_x is more favorable for O_2 adsorption than that in the reduced one in contrast to the case of the Pt/C catalyst.

As mentioned above, it is likely that the reductive electrolysis at potential of -0.6 V forcefully reduces the Ta_2O_5 to Ta species of oxidation states of less than $5+$ but higher than $4+$ and that the thus-electrogenerated species is suggested as TaO_x that contains the so-called oxygen vacancies which have been considered as active sites of O_2 adsorption in metal oxides [7,8] and in addition as active sites for ORR [4,5,16,20]. Oxygen vacancies are also regarded to promote the conductivity of metal oxide [10,11,21]. In addition, the change of TaO_x morphology, i.e., a formation of smaller particles (as seen from the SEM images) which consequently increased the Ta coverage area (as indicated by greater intensity of Ta XPS spectra) by the electrochemical reductive treatment may reduce the insulating property and enlarge the active surface area, as well. Thus, all these led to significant impacts for the ORR activity.

4. Conclusions

We have demonstrated a new technique for preparing a TaO_x-based electrocatalyst for ORR by employing electrochemical reduction. The Ta_2O_5 on the as-prepared deposits was reduced by electrolysis at potential of -0.6 V for 12 h generating a smaller size of deposits. The reduced species could be assigned as Ta_2O_{5-y} ($0 < y < 1$). The treated TaO_x exhibits a high ORR activity in acidic solutions as seen from a fairly high onset potential of 0.87 V. By RRDE voltammetric measurements, it can be concluded that this oxide possesses an almost four-electron ORR electrocatalysis at potential above 0.8 V but its electrocatalysis gradually decreases and a two-electron ORR becomes significant as the potential is increased negatively. The obtained results demonstrate that the present "treated" TaO_x is expected as a promising electrocatalyst for ORR in PEMFCs even though its electrocatalytic performance needs to be improved significantly further to replace the Pt/C.

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